

## Coal Desulfurization During Gaseous Treatment

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Sulfur removal from coal during treatment in gaseous atmospheres at elevated temperatures is of interest both because such a treatment might serve as a basis for a coal desulfurization process and because knowledge of the fate of sulfur under such conditions has application to the behavior of coal during carbonization or gasification. In the work reported here, desulfurization of both a raw and deashed Iowa coal were investigated in three different gases, nitrogen, hydrogen and a 6% oxygen-94% nitrogen gas mixture. With each gas, both the temperature and holding time at temperature were varied. With hydrogen and nitrogen, the temperature was varied between 300 and 700°C. The temperature range used with the oxygen-nitrogen mixture was only from 350 to 455°C due to the large weight loss at higher temperatures caused by combustion of the sample. Holding time at temperature was varied from 0 to 60 min.

### EXPERIMENTAL

The investigation was carried out in a Rigaku CN8001 H type thermal analyzer which included a thermal gravimetric analyzer, a preprogrammed heating unit and temperature control system, and a data recording unit. To carry out a run, about 300mg of coal (<125 $\mu$ ) was placed on the sample pan of the thermal analyzer and heated to the desired temperature using a heating rate of 20°C/min while maintaining a flow of gas over the sample. After holding the sample at temperature for the desired period of time, the gas flow was switched to nitrogen and the reaction chamber was cooled with the initial cooling rate being on the order of 250°C/min. The sample weight was recorded continuously, and at the end of the run the total and organic sulfur contents of the treated coal were determined.

The coal came from the Jude mine, Mahaska County, Iowa, and is a high-volatile-C bituminous coal. The raw coal contained 3.25% inorganic sulfur and 3.04% organic sulfur (moisture-free basis). The deashed Jude coal was prepared by twice floating the raw coal in a heavy liquid medium having a specific gravity of 1.3. It contained 4.74% organic sulfur, but only 0.69% inorganic sulfur. Thus, the results of experiments using the deashed coal manifested largely the behavior of the organic sulfur compounds in the coal. The analyses of the raw and deashed coal are shown in Table 1.

Table 1. Proximate analyses of coal samples

Proximate Analysis	Raw Coal	Deashed Coal
Moisture	1.22%	2.21%
Ash	18.80%	5.54%
Volatile matter	39.68%	45.72%
Fixed carbon	40.30%	46.53%

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## RESULTS AND DISCUSSION

### Effect of Temperature and Holding Time

The effect of temperature upon sulfur removal in each of the three gases was investigated by heating the coal sample to the desired temperature using a heating rate of 20°C/min. followed by immediate cooling. In nitrogen, the amount of sulfur in all forms except for the organic sulfur in the raw coal tended to decrease with increasing temperature, with the decrease being greater for the deashed coal. At 700°C, the total sulfur content of the raw coal and the total and organic contents of the deashed coal were 5.60, 3.27 and 3.05 wt.%, respectively. On the other hand, the organic sulfur content of the raw coal increased from 3.04 to 4.82 wt.% as the temperature was increased from room temperature to 700°C. Since the raw coal contained a substantial amount of inorganic sulfur, this result indicated that inorganic sulfur was being transformed into organic sulfur during the heating process.

The various sulfur contents of the coal samples were not greatly affected when the coal was held at constant temperature. At lower temperatures, the sulfur contents tended to decrease slightly, while they tended to increase when held at higher temperatures.

Fig. 1 shows the effect of temperature on the total and organic sulfur content of the raw and deashed coal when treated with hydrogen. Again, except for the organic sulfur content of the raw coal which increased slightly, the various sulfur contents all decreased with increasing temperature. When the coal was held at temperature for extended periods, there was little change in the sulfur content at temperatures below 600°C. However, at higher temperatures the sulfur content decreased significantly when the sample was held at temperature in hydrogen.

The effectiveness of hydrogen for preferential removal of the organic sulfur can be determined by comparing the differences in the amount of organic sulfur removed during treatment with nitrogen and hydrogen. Any desulfurization in nitrogen is due to the evolution of volatile compounds containing sulfur. Therefore, no matter what the temperature or treatment time, a unique relationship should exist between the organic sulfur removed and the weight loss. The data collected with deashed Jude coal did indeed exhibit such a relationship (Fig. 2).

In hydrogen, sulfur is removed either by devolatilization, as in nitrogen, or by reaction of the hydrogen with sulfur in the organic matrix to form hydrogen sulfide. The effectiveness of hydrogenation for desulfurization can be judged by comparing the organic sulfur removed versus weight loss curves in hydrogen and nitrogen (Fig. 2). Up to a weight loss of about 40% (point A, Fig. 2), the organic sulfur loss curves in the two gases were nearly the same. However, at higher weight losses, the organic sulfur removed in hydrogen increased rapidly with only a slight increase in weight loss indicating that the sulfur-hydrogen reaction was taking place. All the experimental points at weight losses greater than that shown by point A were taken at 600 and 700°C. Reaction of hydrogen with the sulfur in coal appears therefore to be significant only at temperatures above 600°C. At lower temperatures, desulfurization in both hydrogen and nitrogen occur only due to removal of volatile, sulfur-containing compounds. The onset of the hydrogen-sulfur reaction accounts for the reduction of sulfur content with increased holding time at temperatures above 600°C.

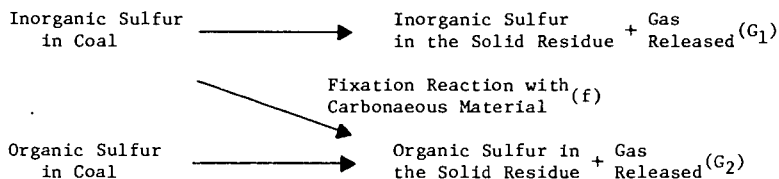
The final gas tested was a mixture of nitrogen with 6% oxygen. The effect on the sulfur content of treatment in the range from 350 to 455°C was slight, with a small decrease in the amount of all forms of sulfur occurring if the coal was held at a temperature in this range. However, the amount of sulfur in the coal decreased fairly substantially as the coal was heated from room temperature to

350°C in an oxidizing atmosphere with the sulfur contents of the two coals at 350°C being as follows:

	Sulfur Content, wt. %	
	Total	Organic
Raw coal	4.77	2.58
Deashed coal	3.87	3.39

#### Transformation of Sulfur

As previously noted, the results of the experiments indicated that some of the inorganic sulfur was trapped by the organic portion of the coal during the heating process. This same phenomenon has been observed by Snow (1) and Cernic-Simic (2). In an attempt to estimate the fraction of inorganic sulfur released as gas ( $G_1$ ) or transformed into organic sulfur ( $f$ ) and the fraction of original organic sulfur released as gas ( $G_2$ ), the following reaction scheme was postulated.



By assuming that this scheme applied to both the raw and deashed coal,  $G_1$ ,  $G_2$  and  $f$  were estimated from sulfur material balances. Details of the calculations are available elsewhere (3).

The fixation reaction, characterized by  $f$ , started at 300°C in nitrogen and increased rapidly between 400 and 500°C with  $f$  reaching 0.7 at 700°C.  $G_1$  was generally small at all temperatures, being between 0 and 0.1.  $G_2$  increased rapidly between 300 and 500°C, and then started to level off between 600 and 700°C. About 70% of the original organic sulfur was released as gaseous compounds at 700°C. In nitrogen, the effect on  $G_1$ ,  $G_2$  and  $f$  of holding time when the sample was kept at constant temperature was small.

The fraction of inorganic sulfur transformed into organic sulfur ( $f$ ) was larger in hydrogen than in nitrogen at low temperatures (Fig. 3). However,  $f$  remained constant at temperatures above 400°C.  $G_1$  was again small, while  $G_2$  increased with increasing temperature as it had in nitrogen.  $f$  and  $G_2$  increased slowly when the samples were held at 400°C, while  $G_1$  remained relatively constant. At 700°C,  $G_1$  and  $G_2$  both increased slightly with holding time, but  $f$  decreased from 0.5 to about 0.2 when the holding time was varied from 0 to 60 min. Apparently the  $H_2S$  formed from the organic sulfur reacted with the iron to produce  $FeS$ .

The fraction of inorganic sulfur transformed into organic sulfur ( $f$ ) in the oxidizing atmosphere was comparable to that in nitrogen at the same temperature. It increased rapidly from about 0.1 at 350°C to 0.36 at 450°C. The fraction of inorganic sulfur released into the gas phase ( $G_1$ ) was much larger than in nitrogen or hydrogen since the reaction of pyrite with oxygen is thermodynamically more favorable than the reaction of pyrite with hydrogen.  $G_1$  was almost unchanged with temperature between 350 and 455°C and was equal to about 0.3.  $G_2$  also was larger in the oxygen-nitrogen mixture and increased rapidly with temperature. About 55% of the organic sulfur was released at 455°C.  $G_1$  and  $G_2$  both increased with holding time at 400°C in the oxidizing atmosphere, while  $f$  decreased as the holding time was increased.

### CONCLUSIONS

Temperature is the most important factor influencing desulfurization in the three gases tested. The holding time at temperature is less important except in the case of hydrogen above 600°C where the sulfur content of the sample decreases with increased holding time. The experimental evidence indicated that this was due to the direct reaction of hydrogen with sulfur in the organic portion of the coal which takes place only at temperatures of 600°C or above. It was observed in the experiments that some inorganic sulfur was transformed into organic sulfur during the gaseous treatment. The fractions of inorganic and organic sulfur released as gases and the fraction of inorganic sulfur transformed into organic sulfur were estimated for each of the gas atmospheres and conditions of temperature and time used.

### Acknowledgement

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### REFERENCES

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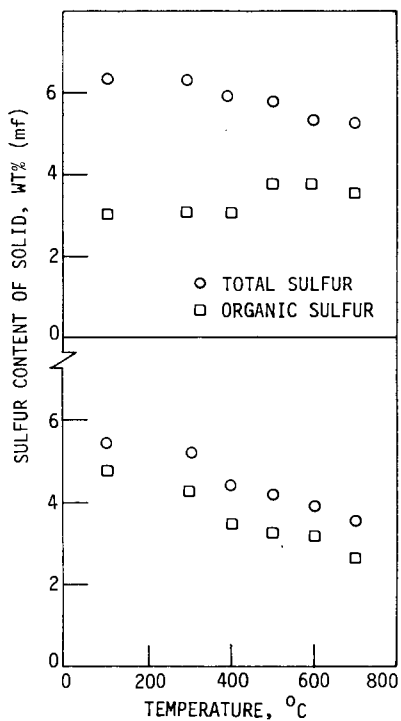


Fig. 1. Effect of temperature on the sulfur content of raw\* and deashed coal heated in hydrogen.

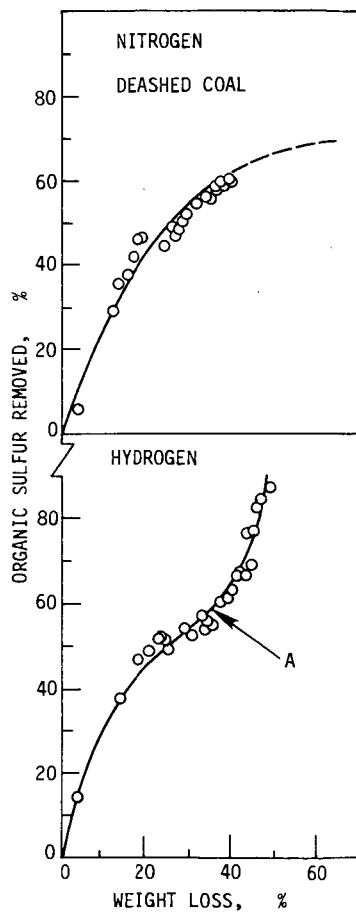


Fig. 2. Organic sulfur removal as a function of sample weight loss for deashed coal.

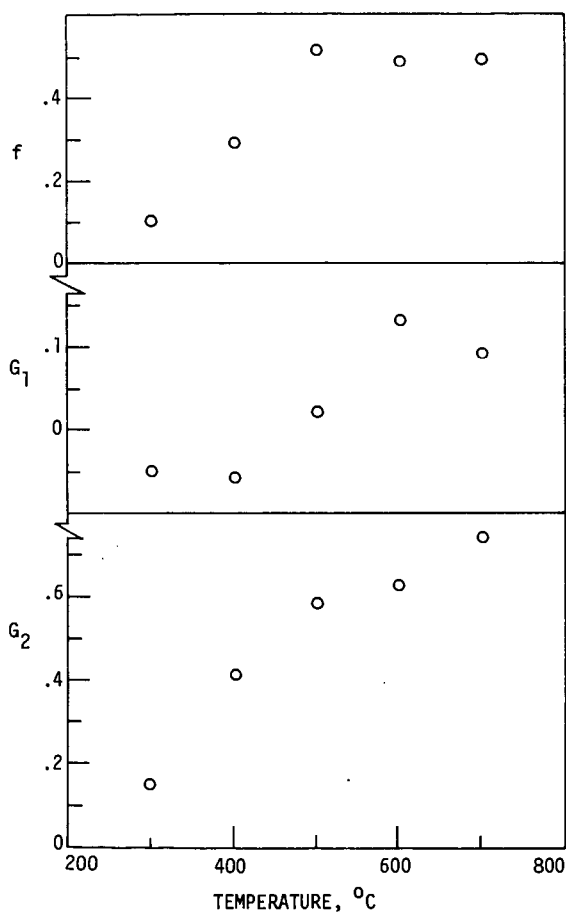


Fig. 3. Effect of temperature on the transformation of sulfur in a hydrogen atmosphere.